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Surface Dynamics of Amorphous Polymers Used for High-Voltage Insulators

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ABSTRACT: Amorphous siloxane polymers are the backbone of high-voltage insulation materials. The natural hydrophobicity of their surface is a necessary property for avoiding leakage currents and dielectric breakdown. As these surfaces are exposed to the environment, electrical discharges or strong mechanical impact can temporarily destroy their water-repellent properties. After such events, however, a self-healing process sets in and restores the original hydrophobicity within some hours. In the present study, we investigate possible mechanisms of this restoration process. Using large-scale, all-atom molecular dynamics simulations, we show that molecules on the material surface have augmented motion that allows them to rearrange with a net polarization. The overall surface region has a net orientation that contributes to hydrophobicity, and charged groups that are placed at the surface migrate inward, away from the vacuum interface and into the bulk-like region. Our simulations provide insight into the mechanisms for hydrophobic self-recovery that repair material strength and functionality and suggest material compositions for future high-voltage insulators.
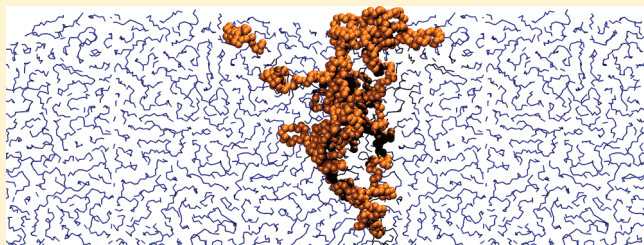
INTRODUCTION

Polymeric materials of poly(dimethylsiloxane) (PDMS) offer adaptable properties such as flexibility or rigidity and thermal and electrical dielectric strength based on the degree of polymerization and on the cross-linking density. Applications range from sensor technology[1] and biomedical devices[2] to materials used for microfluidic channels.[3,4] The focus of this study is on PDMS-based materials that are designed with high dielectric strength as insulators for high-voltage cables.[5] Because these insulating materials are exposed to weather, they must have a surface that is hydrophobic so as to not accumulate polar molecules. Excessive electric fields can cause failure of the insulation properties through oxidization[6−8] and molecular rearrangement.[9] The surface of the insulator then becomes hydrophilic, causing water and other molecules to collect.[10] This, in turn, results in leakage currents and a material that is degraded or destroyed.[6,8,11,12] Self-recovery of the hydrophobic surface usually occurs over a period of hours to days[13] and is based on either diffusion of small molecules to the surface[11,14] and/or surface dipole rearrangement.[12] Material integrity could be significantly improved if this recovery could be accelerated.

Based on PDMS, a rigid amorphous polymer blend is regularly used for industrial applications as high-voltage insulation materials. This material is a mixture of large and small polymeric chains based on a siloxane backbone,[15] and it is similar to the commercial product Sylgard-184 (Dow Corning). Small crosslinker molecules are added to a system with much longer chains, and a chemical reaction is induced to connect these two molecular groups. The result is at least a doubling of the degree of polymerization of the larger molecules, achieving the desired rigidity of the material.

In a recent paper,[16] we studied the dynamics of an amorphous bulk material made of PDMS molecules with full periodicity and found that both the local packing of the material as well as an attractive electrostatic environment were critical factors for short periods (<500 ps) of enhanced molecular motion of smaller molecules. To improve our understanding of the diffusion and polarization at the surface, the present study investigates the structure and dynamics of a similar material with exposure to a vacuum. In addition to exhibiting high dielectric strength, materials for high-voltage insulation are required to be hydrophobic at the surface. We find that fast molecular motion is highly dependent on the proximity of the molecule to surface, an expected result that is important for understanding the hydrophobic self-recovery of this material. After equilibration, the surface was found to have a net polarization based on the molecular rearrangement of methyl groups, a result that is important for understanding the surface hydrophobicity.

Oxidative events damage surface hydrophobicity, and the carbon atoms at cross-linking sites have been proposed as oxidation sites.[6,8] The presence of charged groups at the surface would be one reason for the impaired hydrophobicity, and therefore, we studied the stability and dynamics of oxidized, negatively charged crosslinker molecules. Charged groups were found to rapidly diffuse inward rather than remain exposed at the
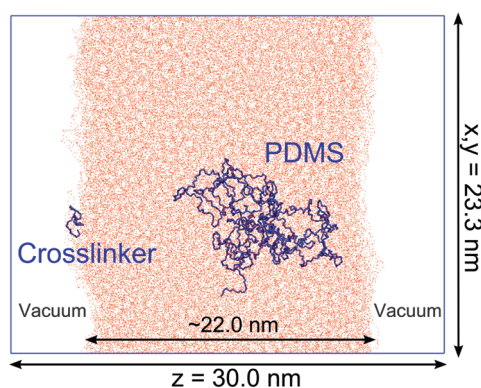
Figure 1. Simulation cell for the surface system at 300 K. The amorphous material is comprised of a mixture of large and small molecules. Representative molecules from the two molecular groups are labeled as PDMS and Crosslinker.

Figure 2. (A) Height–height correlation of surface roughness for the first 25 ns of simulation on the upper surface. At the start of the trajectory, the surface equilibration occurs and is completed by ∼17 ns. (B) Behavior of $H(\mathbf{r})$ for a single time step ($t = 25$ ns) for the upper (blue color) and lower (red color) surface. The inset shows the average rms roughness for both surfaces as a function of time.

surface. Overall, these findings help to explain current material properties and to suggest design choices for future materials with desired properties.

■ METHODS

Model System. Figure 1 shows a cross section of the surface system; the nonperiodic direction includes the vacuum buffer on the horizontal axis. Throughout this article, we will use the Cartesian z coordinate as the nonperiodic direction. Overall, the material was ∼22 nm across, with regions of reduced density at the interface to the vacuum. The periodic x and y directions had a box length of 23.3 nm. The larger molecular type, polydimethylsiloxane (PDMS), had a degree of polymerization (DP) of 978 with vinyl ($-CH=CH_2$) termination. Sixty-seven of these molecules were used, and the molar mass of each was ∼72 500 g/mol. Crosslinker molecules were based on polymethylhydrosiloxane (PMHS) with trimethyl ($-(CH_3)_3$) termination, and 132 of these molecules were included. These molecules were much smaller, with DP = 32 and a molar mass of ∼1960 g/mol. Representative molecules are shown in Figure 1 for size comparison. The total number of atoms in the system was 687 147, which was 67% of the bulk system studied previously.[16] The system can be considered a precursor to a cross-linked system; no reaction was considered because of the increased rigidity and decreased dynamics of the material. It is the purpose of this study to investigate the diffusion of these smaller crosslinker molecules as part of the matrix of the larger, more rigid, PDMS molecules, in the context of the surface system.

Force Field. A force field based on an all-atom classical potential was implemented with LAMMPS code[17,18] on the IBM Blue Gene (BG) supercomputer family.[19] On two dedicated racks of BG/L (11.2 TFLOPS peak), we were able to obtain 4 ns of simulation time per 24 h period, with near-ideal scaling with respect to computational resources. On the basis of the quantum chemical calculations for PDMS materials by Smith et al.,[20] we have used either harmonic or Class II bonding terms.[21,22] A modification to the Class II potential was implemented because of the discontinuity of the energy at the linearization point of the Si–O–Si bond, an approach reported elsewhere[9,20] and described in more detail in ref 16. An integration time step of 2.0 fs and a temperature of 300 K, including a Langevin thermostat with dampening every 10.0 ps, were used for all simulations.
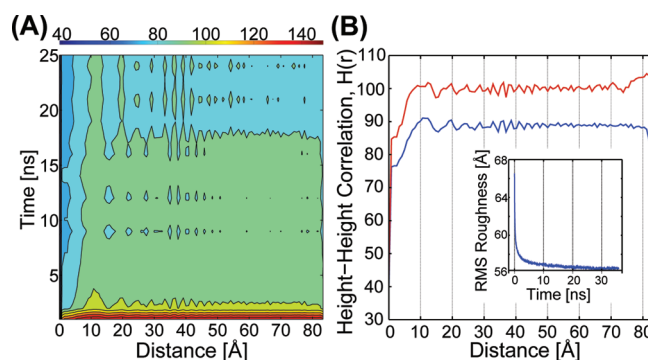
All covalent bonds involving hydrogen were constrained using the SHAKE algorithm.[23] For Lennard-Jones nonbonded interactions, the $1/r^6 + 1/r^{12}$ potential was used and modified to fit the Buckingham potential implemented elsewhere.[20] For Coulombic nonbonded interactions, a standard $1/r$ relationship was used. Both nonbonded interactions were cut off at 10.0 Å, not computed for 1–2 and 1–3 atom pairs, and reduced by half for 1–4 atom pairs. Partial atomic charges were based on ref 20, with the following modifications: terminal vinyl carbon atoms were assigned a charge of $-0.205e$, and on the crosslinker molecules, the nonterminal Si and backbone H atoms had charges of $+0.804e$ and $-0.198e$, respectively. Each molecule was neutral in charge, as was the overall system. The only exception was the case of the simulations with negatively charged molecules described later.

Generation of the Amorphous Surface System. To generate an amorphous structure, we softened the intermolecular potentials to allow accelerated mixing. After mixing, the chemically precise potentials were gradually reintroduced, and the system was fully equilibrated for more than 20 ns. Full details are described in ref 16.

To create a surface system with vacuum boundaries, several steps were necessary. Molecules whose centers of mass were found in the outermost 1/6 of the bulk simulation box were removed. Next, the size of the simulation box that was intended to be the nonperiodic direction (z) was increased to include the unwrapped molecules in that direction. Then, the system was equilibrated at 300 K.

To confirm that the surface was equilibrated properly, we calculated various surface properties. On the basis of the work by Wollschläger et al.,[24] surface morphology analysis was characterized by the height–height correlation, defined as

$$H(\mathbf{r}) = \langle [h(\mathbf{r}' + \mathbf{r}) - h(\mathbf{r}')]^2 \rangle \tag{1}$$

The results of this analysis, shown in Figure 2, indicate that the surface structure can be considered equilibrated after ∼17 ns of simulation. Additionally, the radial height–height correlation approaches 0 for short distances, while for larger distances, $H(\mathbf{r})$ oscillates and approaches $2w^2$, where w is the rms height (see Figure 2B). In addition to the height–height correlation, we calculated the time course of the root-mean-squared (rms) surface roughness (see inset of Figure 2B). The analysis of such
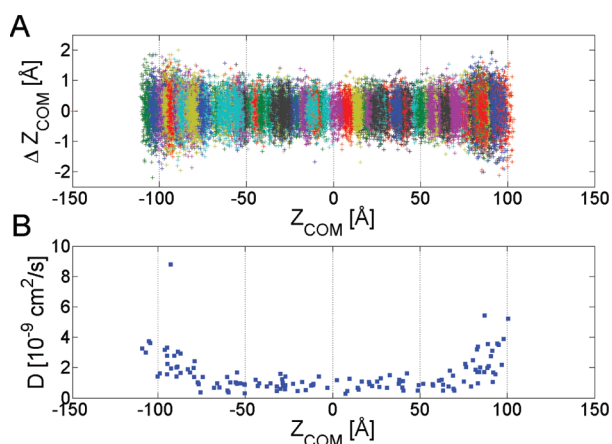
Figure 3. Center of mass coordinate (Z_{COM}), shown for the nonperiodic box position of crosslinker molecules, indicates molecular proximity to the surface. (A) The change in this coordinate over a 10 ps time steps (ΔZ_{COM}) illustrates the increased diffusion of crosslinker molecules at the surface, in this case in the direction perpendicular to the surface. (B) Diffusion coefficients D at 300 K for crosslinker molecules as a function of their final center of mass position in the surface system.

quantities allowed us to validate the equilibration of the trajectories, assessing the reliability of the surface models employed in the diffusivity measurements and in the charge migration calculations. After equilibration, the surface system contained approximately 8 nm of vacuum buffer.

■ RESULTS

Molecules at the Surface Diffuse More. Understanding the rearrangement of molecules that are exposed to a vacuum is important because the equilibrium structure at the surface affects the hydrophobicity, which in turn affects the dielectric strength of the material. Molecules at the interface with the vacuum layer, such as the crosslinker molecule shown in Figure 1, have a reduced number of neighbors because of their partial exposure to the vacuum. After equilibration of the surface system, increased diffusion of crosslinker molecules based on their proximity to the vacuum was observed. As shown in Figure 3A, the diffusion of the center of mass in the nonperiodic direction (z) was largest for molecules on the surface, indicating that they are moving, not surprisingly, inward and outward more than molecules in the central regions do. This motion was calculated for each crosslinker molecule. Crosslinker molecules with increased center of mass motion were located at the surface and had increased exposure to the vacuum.

The molecular motion was quantified by squaring the spatial deviation from the initial coordinates of the equilibrated system (mean squared displacement, or MSD). From the MSD, the diffusion coefficient for a trajectory, or diffusivity (D), may be calculated using the Einstein relation

$$\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 6Dt \qquad (2)$$

where t is the simulation time.[25] Crosslinker molecules diffused considerably faster than the PDMS molecules because of their smaller size, and crosslinker molecules at the surface contribute to a large spread of values for the MSD. Molecular motion of both types of molecules at the vacuum boundary contributed to an increased diffusion constant, especially due to motion in the
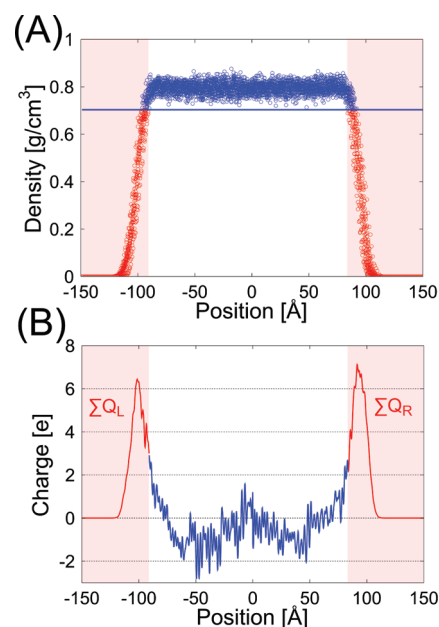

Figure 4. (A) Mass density as a function of box position. Surface regions on the left and right of the system have a reduced density because of the molecular exposure to the vacuum and surface roughness. (B) The partial atomic charges are integrated over the nonperiodic direction and averaged over all equilibrated time steps. The left and right interface regions (ΣQ_L and ΣQ_R) are stable with a positive polarization due to methyl groups pointing outward, a result that is consistent with a hydrophobic surface.

periodic y and z directions. This effect was particularly enhanced for the crosslinker molecules: because of their smaller size they were more likely to be more exposed at the interface. The diffusion coefficients (D) for crosslinker molecules as a function of their center of mass are shown in Figure 3B. Because of their large size, PDMS molecules are likely to have some region exposed to the vacuum. Thus, their diffusion coefficients are highly dependent on the slab width and box dimensions and are not shown. For the smaller crosslinker molecules, there is clear spatial dependence on the MSD: individual molecules near the vacuum region showed increased diffusivity. Due to the asymmetric system, there was anisotropic diffusion. The mean diffusivity in the nonperiodic direction (z) was 4.2×10^{-9} cm^2/s, and in the periodic directions (x,y) the mean was 1.1×10^{-8} cm^2/s. PDMS molecules had a similar distinction between nonperiodic and periodic diffusivity: 2.3×10^{-9} and 5.5×10^{-9} cm^2/s, respectively. The proximity to the surface was the determining factor for the magnitude of self-diffusion of an individual molecule. The proximity effect contributed to enhanced diffusion more so than electrostatic causes that had been identified for the bulk system with uniform density.[16]

Polarization at the Surface Caused by Molecular Order. The nonuniform density profile, shown in Figure 4A, identifies the interface regions on the left and right that are exposed to the vacuum. These regions have an average density for the entire trajectory that is lower than 88.5% of the mean density in the bulk-like, central region. The interface regions consisted of the outermost molecules that, on average, extended ~15 Å from the center region. To quantify the surface polarization, the partial atomic charges were considered as a function of their Cartesian position in the nonperiodic direction (z). The atomic charges for

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atoms in the left and right interface regions were integrated over all equilibrated time steps. A net polarization was observed as a function of the box position and based on proximity to the vacuum, as shown in Figure 4B. The left and right surface regions had a significant net positive polarization, specifically, $\Sigma Q_L = +21.3e$ and $\Sigma Q_R = +29.3e$, and the compensating negative charge was distributed over the central region.[26] When normalized, the charge per area on the left and right surface regions was $+6.2 \times 10^{-3}$ and $+8.6 \times 10^{-3}$ C/m^2, respectively. The presence of positively polarized surface regions indicated that the molecules on the surface underwent reorientation to stabilize their vacuum-exposed groups and that, in contract to the bulk material, charged or polar groups would have distinct interactions with the surface.

To understand the polarization at the surface, the structural orientation of both PDMS and crosslinker molecules was investigated. The magnitude of the orientation order parameter (S), defined as

$$S(z) = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle \qquad (3)$$

where θ is the angle between the vector of molecular orientation and the unit vector $\hat{z}$ normal to the surface, was averaged over the equilibrated trajectory in the nonperiodic direction (z).
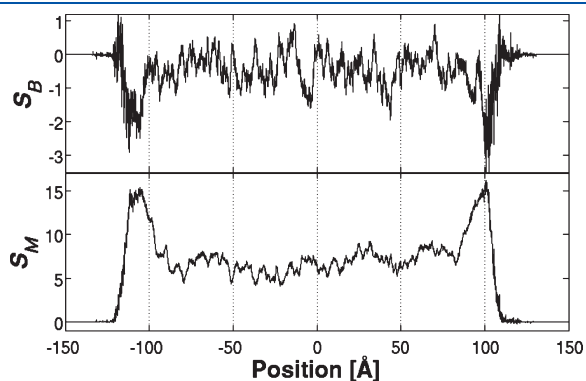

Figure 5. Orientation order parameters at a temperature of 300 K, as a function of box position and scaled by a factor of 1000. The backbone (top, S_B) and methyl (bottom, S_M) order parameters are nonzero at the interface and show a negative correlation, indicating a surface region with molecular order and a hydrophobic surface.

The order parameter for backbone groups, S_B, is based on the vector between two silicon atoms separated by two oxygen atoms ($Si_i - Si_{i+2}$). The order parameter for methyl groups, S_M, is based on the vector between a silicon atom and a methyl group or a hydrogen in the case of the Si—H bonds on the crosslinker molecules. Ismail et al. showed that for a smaller, PDMS-based interface system similar order parameters are nonzero.[27] In particular, they showed that S_B and S_M are negatively correlated at the interface because of a positive S_M (perpendicular alignment) and a negative S_B (parallel alignment). Our results for a larger system with mixed PDMS-based components are in agreement and are shown in Figure 5. The nonrandom order of molecular groups at the surface provides a structural explanation for the charge polarization shown in Figure 4B. Specifically, the nonpolar methyl groups pointed outward,[28] a result that is consistent with experiment[29] and that suggests the dynamics for polar and charged groups at the surface.

Ionized Groups Diffuse Away from the Surface. The surface was found to consist of exposed methyl groups that contribute to hydrophobicity, a desired surface orientation. We propose that the presence and stability of a hydrophobic surface would drive a charged molecule inward, thus repairing the hydrophobicity. To test the effect of a hydrophobic surface on the molecular dynamics, we considered a set of charged crosslinker molecules. The carbon—carbon bond located at cross-linking sites between PDMS and crosslinker molecules was experimentally determined to be the site for oxidation.[6,8] For the set of charged crosslinker molecules, one terminal methyl group was changed to a carboxylate group ($-COO^-$). The net charges of that terminal group and of the entire molecule were $-1.0e$. In addition, a crosslinker molecule with negative charges on both termini was considered. Charged crosslinker molecules were added at various proximities to the surface and with various starting configurations, either buried or exposed. By adding charge, we investigated whether individual charged groups were more stable at the surface boundary or embedded inside the material.

We found that negatively charged groups consistently migrated inward with a higher rate than noncharged molecules. In addition, the inward motion of charged groups was faster than the motion of the center of mass diffusion of that particular molecule. Once equilibrated and away from the surface, charged groups became stabilized and did not diffuse back to the surface.
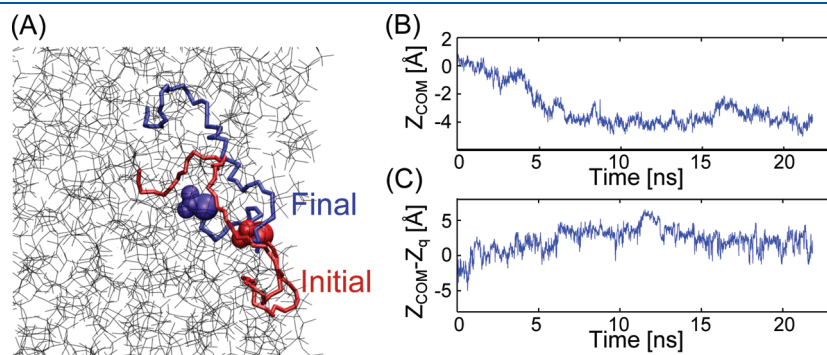

Figure 6. Charged molecules that start at the surface migrate inward so that the charged group is buried in the material. (A) A charged group (spheres) is shown for a representative crosslinker molecule (tubes) at the initial (red) and final (blue) equilibrated position. (B) The center of mass in the nonperiodic direction (Z_{COM}) for such a molecule is shown with respect to the initial position. A negative value indicates inward motion, away from the surface. (C) The distance between the molecule's center of mass (Z_{COM}) and the charged group (Z_q) is shown for the entire trajectory. The change in sign, from negative to positive, at the beginning of the trajectory indicates that the charged group moved inward more than the entire molecule did during the equilibration process.

The energetic stability gained when the charged group was buried overcame any attractive forces that would hold the charge group at the surface.

A representative molecule is depicted in Figure 6A, where the inward migration is shown as initial and equilibrated coordinates for a crosslinker molecule with a negatively charged group. During the trajectory, the z-coordinate of the center of mass for the molecule indicated that diffusion was inward and away from the surface, as shown in Figure 6B. In addition, the charged group, which was placed on the surface, moved faster toward the central region than the entire molecule. This motion is illustrated in Figure 6C, where the z-coordinate of the charged group is subtracted from the center of mass of the molecule. A change of sign in this quantity was observed at around 1 ns into the trajectory, which indicates that the charged group moved inward more than the entire molecule. Similar results were found for other charged groups placed at the surface. For the migrating charged molecules, the potential energy from Coulomb interaction was found to be stabilized by approximately 41 ± 8 kcal/mol.

Negatively charged groups at the surface were less stable and preferred to be buried in the material. The directed diffusion of charged molecules away from the surface is consistent with the presence of a stable surface region that is polarized because of the ordering of the hydrophobic groups that are exposed. After an oxidative event, the migration of charged molecules away from the surface suggests a potential mechanism for self-recovery of the hydrophobic surface.

■ CONCLUSION

In summary, we have simulated the molecular dynamics of an amorphous, polymeric surface system that is of interest as a material for high-voltage insulation. Because high-voltage insulating cables may experience dielectric breakdown that leads to leakage currents, the self-recovery of surface hydrophobicity is an essential property. Molecules on the surface experienced faster diffusion because they had fewer neighbors, which allowed an orientation that was not present in the bulk material. In this way, the surface had a structural configuration that caused a net polarization due to ordering of the methyl groups. That is consistent with a hydrophobic surface. The stability of charged molecules was investigated, and these molecules were found to be more energetically stable when buried in the "bulk-like" material rather that at the surface. Because smaller molecules diffuse faster, their diffusion in the direction perpendicular to the surface as well as their hydrophobicity will be important factors for the self-recovery of the dielectric strength of high-voltage insulators. Future materials could thus include relatively small, nonpolar molecules, which are more susceptible to oxidation. In the uncharged state, these molecules diffuse to the surface because of their faster diffusion, so that surface hydrophobicity remains intact. If they are charged, and especially if they are preferentially oxidized, they would diffuse away from the surface more rapidly and therefore contribute to the self-repair mechanism. Such molecules would contribute to the desired dielectric properties regardless of their proximity to the surface.

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dx.doi.org/10.1021/jp207589p |*J. Phys. Chem. B* XXXX, XXX, 000–000